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<b>(21) International Application Number:</b> PCT/US99/21709 <b>(22) International Filing Date:</b> 20 September 1999 (20.09.99)  <b>(30) Priority Data:</b> 09/157,845 21 September 1998 (21.09.98) US 09/379,883 24 August 1999 (24.08.99) US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> LEE, Yann-Per; 6386 Kings Arms Way, Fairfield, OH 45014 (US). FRANCE, Paul, Amaat; 8375 Todd Creek Circle, West Chester, OH 45069 (US). RADOMYSEL- SKIY, Arseniy; Apartment 3, 2940 Portsmouth Avenue, Cincinnati, OH 45208 (US).  <b>(74) Agents:</b> REED, T. David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (Utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> DURABLY WETTABLE, LIQUID PERVIOUS WEBS  <b>(57) Abstract</b>  Disclosed are durably wettable, liquid pervious webs that are particularly useful as topsheet materials for absorbent articles, such as baby and adult diapers, feminine hygiene products and the like. The durably wettable, liquid pervious webs are formed by applying a relatively permanent hydrophilic coating onto at least one surface of a web (a polymeric film or nonwoven) via plasma polymerization. Also disclosed are absorbent articles which include the durably wettable, liquid pervious webs as a topsheet, as well as the plasma polymerization process for making the durably wettable, liquid pervious webs.		

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**DURABLY WETTABLE, LIQUID PERVIOUS WEBS**

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**CROSS REFERENCE TO RELATED APPLICATIONS**

This is a Continuation-in-Part of co-pending application Serial No. 09/157,845 filed September 29, 1998.

**TECHNICAL FIELD**

10       The present invention relates to a durably wettable, liquid pervious web that is particularly suitable as a topsheet for absorbent articles. More particularly, the invention relates to a polymeric film or nonwoven to which is applied a thin coating of organic material onto at least one surface of the film or nonwoven. The thin organic coating is applied by a plasma-induced chemical vapor deposition process. The thin organic coating renders the web more permanently hydrophilic than other methods known in the art. The invention further relates to a process for making the durably wettable, liquid pervious web, and to articles containing the durably wettable, liquid pervious web as a topsheet.

**BACKGROUND OF THE INVENTION**

     Polymeric and nonwoven webs are common components of disposable absorbant articles, dryer sheets and the like. More particularly, macroscopically expanded, three-dimensional, polymeric films have been utilized as topsheet materials for disposable absorbent articles. As used herein, the term "macroscopically expanded", when used to describe three-dimensional webs, refers to webs which have been caused to conform to the surface of a three-dimensional forming structure so that both surfaces thereof exhibit the three-dimensional pattern of the forming structure or webs that have an inherent three-dimensional pattern arising from their structure. Regardless of whether the three-dimensional pattern is inherent or generated by application of a forming process, the pattern is readily visible to the naked eye when the perpendicular distance between the viewer's eye and the plane of the web is about 12 inches. By way of contrast, the term "planar", when utilized herein to describe nonwovens and polymeric films, refers to the overall condition of the web when viewed by the naked eye on a macroscopic scale. In this context "planar" webs may include webs having fine-scale surface aberrations on one or both sides, the surface aberrations not being readily visible to the naked eye when the perpendicular distance between the viewer's eye and the plane of the web is about 12 inches or greater.

     One macroscopically expanded, three-dimensional apertured polymeric web which is particularly well suited to transferring liquid deposited on one surface thereof to its opposite surface and thereafter isolating the transferred liquid from a wearer's skin is disclosed in commonly assigned U.S. Patent No. 3,929,135 issued to Thompson on Dec. 30, 1975, the disclosure of which is incorporated by reference

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herein. Thompson describes a macroscopically expanded, three dimensional web (e.g., a topsheet) comprised of liquid impermeable material, but provided with a pattern of tapered capillaries, the capillaries having a base opening in the plane of the topsheet and an apex opening remote from the plane of the topsheet, the apex opening being in intimate contact with the absorbent pad utilized in the disposable  
40 absorbent article. The Thompson topsheet allows the free transfer of liquids from the wearer's body into the absorbent element of the device while inhibiting the reverse flow of these liquids. This provides a relatively much drier surface in contact with the user than had previously been obtainable. Another macroscopically expanded, three-dimensional apertured plastic web well suited for use as a topsheet on absorbent articles such as sanitary napkins is disclosed in commonly assigned U.S. Patent No. 4,342,314 issued to Radel et al.  
45 on Aug. 3, 1982, the patent being hereby incorporated by reference herein. The macroscopically expanded, three-dimensional plastic web disclosed in the Radel patent exhibits a fiber-like appearance and tactile impression which has been favorably received by consumers when used as a wearer contacting surface. According to the teachings of the commonly assigned patents to Thompson and to Radel, et al., plastic webs of the aforementioned type can be made by applying a pressure differential to the web while it is supported  
50 on a three-dimensional forming structure until the web is macroscopically expanded to comply with the three-dimensional cross-section of the forming structure on which it is supported. When aperturing of the macroscopically expanded, three-dimensional web is desired, the pressure (vacuum is described) differential is applied continuously until such time as aperturing of the web in areas coinciding with the apertures in the forming structure has been completed.

55 A multi-phase, liquid-based process such as that described in U.S. Patent No. 4,609,518, issued September 2, 1986 to Curro et al. (hereafter referred to as "518 patent"), was also developed to provide a film with very small and very large apertures immediately adjacent one another. As the patent discloses, the formation of the very small (including micro-sized) apertures in the direction opposite those formed for large apertures hinders the ability of initially unabsorbed liquid from running off the web's surface. Thus,  
60 liquid not immediately transported through the large apertures is restrained from running off the web's surface, and is subsequently taken up through the larger apertures and is deposited in the article's core where the web is used as a topsheet material. These outwardly formed small apertures also reduce the level of web/skin contact and reduce the rigidity of the film, and thereby feel more comfortable to the user. Wearers have reported that such topsheets have a soft silky surface. Alternatively, the '518 patent discloses  
65 films where the very small apertures are formed in the same direction as the macro-apertures.

Regardless of the means employed for aperture formation, where a wettable film material is desired, the above references generally obtain such a structure by surface treating the naturally hydrophobic polymeric web with a wetting agent. Surface treatment is generally accomplished by either spraying surfactant onto the web's surface or by dipping the web in a surfactant-containing bath. Regardless of  
70 which of these methods is employed, surface treatment suffers from the inability to precisely control the location and level of treatment, as well as adverse effects caused by migration of significant amounts of surfactant into apertures and other components (e.g., absorbent core) when the apertured film is used as a topsheet in an absorbent article. Surface treatment further suffers from the disadvantage that desirable

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75 wetting agents, or surfactants, tend to be washed off upon repeated exposure to such liquids. Thus, when used as a topsheet in an absorbent article, the treated films lose their ability to transport liquid away from the skin and into the article's core after repeated wettings.

U.S. Patent No. 4,535,020, issued to Thomas et al. on August 13, 1985, addresses some of the problems associated with surface treating vacuum-formed apertured films by incorporating hydrophilic surfactant in the polymeric resin before extrusion for film formation (referred to herein as "resin incorporated surfactant", or "RIS"). (See also commonly assigned U.S. Patent Application Serial No. 08/713,377, filed September 13, 1996 by Y. P. Lee, et al.; U.S. Patent No. 4,923,914 to Nohr et al., issued May 8, 1990; U.S. Patent No. 5,057,262 to Nohr et al., issued October 15, 1991; U.S. Patent No. 5,120,888 to Nohr et al., issued June 9, 1992.) According to the teachings of Thomas, after extrusion of the resin/surfactant mixture, and subsequent formation of the apertures, the incompatible surfactant eventually blooms to the film's surface to provide a more durably wettable web. However, as with surface treatment, RIS suffers from some degree of surfactant wash-off during use and/or during manufacture, particularly if liquid pressure differentials are used to form the web's apertures. Also, hydrophilic webs formed using RIS techniques are not immediately wettable, and depending on the relationship between the resin and the surfactant and environmental conditions, may not become wettable for finite periods of time. Similarly, when such webs are used in absorbent articles, there will be some time delay before surfactant (that is washed off during wear) is replenished at the web's surface.

In spite of the teachings of the prior art, there remains a need for a liquid pervious web or film material that offers improved durable wettability after the passage of time and/or after exposure to liquid insults. Such materials have particular suitability for use in disposable absorbent structures. There also remains the need for a process that provides such a durably wettable, liquid pervious web.

Accordingly, it is an object of the present invention to provide a liquid pervious web having improved durable wettability. This durable wettability is attained by applying a plasma-induced hydrophilic coating onto at least one surface of the starting web, to render the resulting web durably hydrophilic.

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### SUMMARY OF THE INVENTION

The present invention relates to a durably wettable, liquid pervious web that is particularly useful as a topsheet material for absorbent articles. In one respect, the invention relates to a durably-wettable, liquid pervious web which comprises:

- 105 (i) a web selected from the group consisting of polymeric films and nonwovens;
- (ii) a substantially continuous hydrophilic coating, less than about 2.5 microns thick, on at least one surface of the web, wherein said hydrophilic coating is applied to the web by plasma polymerization;

wherein at least one surface of the durably-wettable, liquid pervious web has a Post Aging contact angle

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110 that is not more than about 60 degrees greater than the Pre Aging contact angle.

In a similar aspect respect, at least one surface of the treated web will have a Post Washing contact angle that is not more than about 60 degrees greater than the Pre Washing contact angle. Preferably, both conditions will exist in a single web.

115 The invention also relates to an absorbent article comprising a durably wettable, liquid pervious topsheet, the topsheet comprising a web and a hydrophilic coating on at least one surface of the web, wherein the hydrophilic coating is applied to the substrate by plasma polymerization.

Finally, the invention relates to a plasma polymerization process for making the durably wettable, liquid pervious webs described herein.

#### DETAILED DESCRIPTION OF THE INVENTION

120 I. Durably Wettable, Liquid Pervious Webs

As discussed in detail below, the present invention relates to a durably wettable web that is prepared by applying a hydrophilic coating to a starting polymeric film or nonwoven, using a plasma polymerization process.

125 As used herein, the term "web" refers to the starting substrate (i.e., a polymeric film or nonwoven) to which the hydrophilic coating is applied. In contrast, the terms "durably wettable, liquid pervious web" or "treated web" refer to the final product - the polymer film or nonwoven having the durable hydrophilic coating.

130 As used herein, the term "liquid pervious" refers to the ability of a web or treated web to transport liquids from one surface of the web or treated web to the opposite surface of the web or treated web in a sufficiently efficient manner so as to allow the treated web to be used as a component of a disposable article. Webs may be inherently liquid pervious or may be made liquid pervious by application of a processing step, such as, aperturing.

As used herein, the term "substantially continuous" means sufficiently continuous to provide the hydrophilic or wettable properties as defined by the stated or claimed contact angle limitations.

135 As used herein, the terms "hydrophilic" and "wetable" are used interchangeably and refer to surfaces that are wettable by aqueous liquids (e.g., aqueous body liquids) deposited on these surfaces. Hydrophilicity and wettability are typically defined in terms of contact angle and the surface tension of the liquids and solids involved. This is discussed in detail in the American Chemical Society publication entitled Contact Angle, Wettability and Adhesion, edited by Robert F. Gould (Copyright 1964). A web surface is said to be wetted by a liquid (i.e., hydrophilic) when either the contact angle between the liquid and the web surface is less than 90°, or when the liquid tends to spread spontaneously across the surface of the web, both conditions normally co-existing. Conversely, a surface is considered to be hydrophobic if the contact angle is greater than 90° and the liquid does not spread spontaneously across the surface of the web. In general, the lower the contact angle between the surface and the liquid, the more hydrophilic the surface.

145 The durably wettable, liquid pervious webs of the present invention are "durably wettable", in as far as the hydrophilic character engendered to the otherwise more hydrophobic film is maintained over time

and after exposure to liquids. As discussed above, prior approaches directed at making hydrophobic films wettable result in initial improvements in wettability, but suffer from the negative attribute that wettability is lost over time and/or exposure to liquids. While not being bound by theory, it is believed that typical hydrophilic polymer and surface-treated polymer systems, such as corona discharge treatments, go through a "hydrophobic recovery" process. During the hydrophobic recovery process, surface wettability tends to decay over time because thermodynamics favors the exposure of lower surface energy molecular chain segments at polymer surface. Upon aging, hydrophilic molecular segments reorient and embed themselves and expose hydrophobic segments at polymer surface. If chemical crosslinking is induced at the polymer surface, the crosslinking tends to limit polymer chain mobility, thus significantly slowing the "hydrophobic recovery" process and therefore preserving polymer surface wettability over time. Since Applicants' invention provides for polymer chemical crosslinking, via a radiation curing process, a durably wettable, liquid pervious web can be produced.

Durable wettability is described herein in terms of the ability of a durably wettable, liquid pervious web (as indicated, also referred to herein as a "treated web", to distinguish from the starting more hydrophobic "web") to retain its wettable character after aging (referred to as "Post Aging") and/or after exposure to liquids (referred to as "Post Washing"). The methods for measuring Post Aging contact angle and Post Washing contact angle are discussed below.

As indicated, the durable wettability of the present durably wettable, liquid pervious webs is attained by use of a plasma process. Plasma is often referred to as the fourth state of matter. When energy is applied to a solid (e.g., a polymeric film or nonwoven), the solid can undergo a transition to the liquid state. If further energy is applied, the liquid becomes a gas. If additional energy of the proper kind is applied, the gas dissociates and becomes plasma. Plasmas exist in a variety of forms. The preferred plasma useful herein is a low pressure or vacuum process, which allows processing of the web at or near ambient temperature, i.e., about 20°C. This prevents thermal degradation of the web being processed and/or thermal distortion of the formed web that is being treated. Within the plasma chamber where the web is to be treated, active species in the form of electrons, free-radicals, ions and energetic neutrals collide with the surface of the web, e.g. polymer, breaking molecular bonds and creating new functional groups on the surface. These active and energetic species also react in the gas phase, resulting in a thin coating being deposited on at least one surface of the web.

Suitable plasma systems for use in the present invention incorporate a parallel plate electrode design where materials to be treated are exposed directly to the primary field of RF energy, but are not part of the circuitry. The subsequent primary plasma is particularly more uniform and more efficient since the part is exposed in all three dimensions to the glow discharge. With higher pressure processes (but still within the general definition of a cold gas plasma), some form of gas delivery system, designed to create a uniform laminar flow of process gas throughout the entire chamber volume is beneficial. In multiple electrode/shelf designs, it is important that each of the electrodes receive equal amounts of RF energy. In this manner a uniform glow discharge is created between each shelf or in each plasma zone. Solid state components and microprocessor control of the system parameters of process time, flow rate, power level,

185 and working pressure, will also ensure process uniformity, efficiency, and repeatability.

Since plasmas are electrically conductive atmospheres, they carry a characteristic impedance to the output of the RF generator. Therefore, the preferred plasma process utilizes a matching network to constantly tune the plasma impedance to the output impedance of the RF generator. Advanced plasma systems suitable for use in the present invention are available from HIMONT Plasma Science, Foster City, Calif. (a business unit of HIMONT U.S.A., Inc.), and incorporate an automatic matching type of network and provisions for error checking during the process.

The low temperature plasma is generated in a gaseous atmosphere at reduced pressure of from about 0.001 to about 10 Torr, preferably from about 0.01 to about 5 Torr, more preferably from about 0.05 to about 1 Torr, and most preferably from about 0.05 to about 0.4 Torr. The electric power can be supplied to the equipment at a high radio frequency, from about 40 KHz to about 3 GHz, preferably from about 13 to about 27 MHz, and most conveniently at about 14 MHz. To achieve the desired plasma condition in the gaseous atmosphere, the electric power delivered to the apparatus can vary over a range of from about 10 to about 10,600 watts; preferably from about 50 to about 5,000 watts, more preferably from about 250 to about 3000 watts, most preferably from about 500 to about 2500 watts. The power used is somewhat dependent on the chamber's working volume. The most preferred range of about 500 to about 2500 watts is appropriate for HIMONT Plasma Science PS0500D gas plasma apparatus with a working volume of about 5.0 cubic feet. The plasma treatment time varies from a few seconds to several minutes, preferably from about 20 seconds to about 30 minutes, most preferably from about 60 seconds to about 20 minutes.

It should be appreciated that treatment pressure, time and power are interrelated, rather than independent, variables. The effect of the level selected for each of these variables will determine the extent of web surface modification and/or coating thickness; also related are the chamber volume and geometry as well as the sample size and surface geometry. The selection of the level for these variables is well within the ordinary skill of practitioners in the art to which this invention pertains.

The hydrophilic coating layer is deposited onto the surface of a suitable web (either previously apertured or unapertured) by low temperature plasma-induced vapor deposition (i.e., polymerization) of a monomer or a combination of monomers, such that a hydrophilic coating will be applied to the web. In a preferred embodiment, the monomers will be silicon-containing compounds having one to three silicon atoms, which compounds are selected from the group consisting of (i) silanes of the formula  $\text{SiR}_4$ , where each R is the same or different and is selected from H; a  $\text{C}_1$ - $\text{C}_8$  linear or branched alkyl or alkoxy; a  $\text{C}_6$ - $\text{C}_{10}$  aryl, unsubstituted or substituted with  $\text{C}_1$ - $\text{C}_8$  linear or branched alkyl; a vinyl radical, i.e.  $-\text{CH}=\text{CH}_2$ ; or a  $\text{C}_3$ - $\text{C}_8$  allyl radical; provided that when R is H only one or two Rs are H; (ii) organosilicones based on a structure consisting of alternate silicon and oxygen atoms with various organic radicals attached to the silicon having the formula  $\text{R}'\text{R}''\text{R}'''\text{Si}[-\text{O}-\text{Si}(\text{R}')(\text{R}'')-]_n-\text{R}'''$ , where  $\text{R}'$ ,  $\text{R}''$  and  $\text{R}'''$  can be the same or different and are  $\text{C}_1$ - $\text{C}_8$  linear or branched alkyl or alkoxy,  $\text{R}'$  and  $\text{R}''$  can also be hydrogen provided that no more than 50% of the  $\text{R}'$  and  $\text{R}''$  groups are hydrogen, and n is 1, 2 or 3; and (iii) mixtures thereof.

Representative silicon compounds include, but are not limited to, hexamethyldisiloxane (HMDSO), methyltrimethoxy silane (MTMS), vinyltrimethoxy silane (VTMS), vinyltriethoxy silane



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(VTES), ethylmeth xy silane (EMS), ethyltrimethoxy silane (ETMS), tetraeth xy silane (TES), cyclohexylmethyl-dimethoxy silane (CMDMS), dicyclopentyl-dimethoxy silane (DCDMS), phenyltriethoxy silane (PES), diphenyldimethoxy silane (DPDMS), tetramethyldisiloxane (TMDSO), and hexamethyltrisiloxane (HMTSO). The silicon compounds employed are introduced into the plasma deposition chamber in the gaseous state. Prior to being introduced into the chamber, the silicon compound is heated to a temperature of from about 40° to about 100°C, generally from about 40° to about 60°C, to vaporize the compound and create sufficient vapor pressure such that the coating is deposited at a reasonable speed. Oxygen in gaseous form and argon are fed into the deposition chamber simultaneously with, but each with a separate feeding means and mass flow controller, the gaseous silicon compound. Depending upon the application, the O<sub>2</sub> flow rate ranges from about 25 standard cubic centimeter/minute ("sccm") to about 1200 sccm, the gaseous silicon compound flow is from about 10 sccm to about 250 sccm, and Ar flow is from about 1 sccm to about 150 sccm. Argon is used to enhance the rate of deposition of the gaseous materials being employed and, therefore, it is preferable to use Argon in the process. With respect to the flow rates for argon and oxygen versus the monomer (e.g. HMDSO) flow rate, the following are preferred: assuming that the mass flow Q1 represents 3% argon and 97 % oxygen and vapor mass flow Q2 represents the mass flow for the monomer, the preferred ratio of Q1:Q2 is from about 10:1 to about 1:2, more preferred is from about 5:1 to about 1:1, and most preferred is about 3:2.

Oxygen is essential to the plasma deposition process with the silicon compounds according to this invention. Without oxygen, it is not possible to obtain a plasma-induced hydrophilic coating using the aforementioned silicon compounds. Whatever oxidizing effect it has, it appears to be necessary to utilize oxygen if one is to obtain the hydrophilic coatings of this invention.

The total vapor pressure of the gaseous materials introduced into the plasma deposition chamber for the deposition of the hydrophilic coating layer is about 0.04 to about 0.5 Torr, preferably about 0.35 to about 0.45 Torr, most preferably about 0.4 Torr. The process pressure must be such that a low bias potential on the RF-driven electrode is achieved. The total vapor pressure for the hydrophilic coating layer is from about 0.04 to about 0.4 Torr, preferably from about 0.06 to about 0.13 Torr, depending on the process used and the substrate being treated.

Alternatively, monomer deposition may be achieved via the flash vaporization technique that is described in U.S. Patent No. 4,842,893 issued to Yializis on Apr. 29, 1988, the disclosure of which is incorporated by reference herein.

The web to be subjected to plasma polymerization may be flat (two dimensional) or complex (three dimensional, including previously apertured films and nonwovens). That is, plasma treatment may be conducted either before or after formation of the apertures of the web. In a preferred embodiment, plasma treatment will be conducted after aperture formation, so as to better preserve a uniform hydrophilic coating on the web's surface.

The aforementioned advanced plasma systems available from HIMONT Plasma Science, such as the PS0500D reactor are equipped with a throttle valve, thereby making it possible to achieve a range of process pressures with the same gas flow rate.

The plasma treatment time for obtaining the desired hydrophilic coatings is from typically about 1 minute to about 10 minutes, preferably about 1.5 to about 4 minutes, most preferably about 1.5 to about 2.5 minutes; and the RF power used to cause reaction of the vapor is typically from about 200 to about 1500 watts, preferably about 1000 to about 1400 watts, most preferably about 1100 to about 1300 watts. The RF power typically employs ranges from about 1200 to about 2500 watts and depends on the substrate being treated and the throughput requirements. The resulting hydrophilic coatings can be produced in different thicknesses, but are typically from about 0.1 to about 2.5 microns, preferably about 1 to about 2 microns.

As indicated, the plasma induced hydrophilic coating exhibits a contact angle for water of less than about 90 degree, such that any water placed on the treated web will tend to spread spontaneously over the treated web's coated surface. In a preferred embodiment, the treated web may be further treated by exposure to a low temperature plasma gas composition (also referred to herein as a "surface modifying gas stream") or an energy source (also referred to herein as "radiation curing") such as an apparatus that emits, including but not limited to, infra red, electron beam, thermionic or ultra violet radiation. Apparatuses that are suitable as energy sources in the present invention are disclosed in U.S. Patent No. 4,842,893 issued to Yializis on Apr. 29, 1988, the disclosure of which is incorporated by reference herein.

In the surface modifying gas stream embodiment the gas stream preferably comprises  $N_2O$  and  $CO_2$ , to enhance the durability of the hydrophilic coating. In one such preferred embodiment, the plasma gas composition will comprise from about 80 to about 40 mol %  $N_2O$  and from about 20 to about 60 mol %  $CO_2$ , preferably from about 70 to about 45 mol %  $N_2O$  and from about 30 to about 55 mol %  $CO_2$ , most preferably from about 60 to about 45 mol %  $N_2O$  and from about 40 to about 55 mol %  $CO_2$ , where the amount of  $N_2O$  and  $CO_2$  in the mixture equals 100 to 10 mol %, for a time sufficient to modify the surface of the hydrophilic coating to enhance its durability.

In the radiation curing embodiment, the radiation source is preferably a gas discharge electron beam gun. The gun directs a flow of electrons through a emitter window onto the monomer, thereby further curing the monomer, which enhances the durability of the hydrophilic coating. Curing is controlled by matching the electron beam voltage to the dielectric thickness of the monomer coating. For example, a 10 Kv electron voltage will penetrate about 1 micron of deposited monomer.

The plasma process is generally practiced as follows. The starting web to be treated is placed into a vacuum chamber and the chamber pressure is reduced, typically to about 0.005 Torr. The process gas or gas mixture employed is introduced to the chamber and the chamber pressure is stabilized at a pressure of 0.04-0.4 Torr. The interior dimension of the work area is approximately 1.73 X 0.76 X 1.02 meters (width x height x depth) for a total working volume of 1.34 cubic meters. A suitable high frequency form of energy, typically 13.56 MHz radio frequency energy, is used to create the plasma; in the system described, this is achieved with a total power input capacity of up to 2500 watts. The RF energy dissociates the gas, creating a plasma characterized by a distinctive glow. Since the process is conducted at reduced pressures, the bulk temperature of the gas is near ambient temperature, thus the reference to a cold gas plasma, a glow discharge, or a cold gas glow discharge. Because the web being subjected to the plasma conditions is located within the electric field, the process is referred to as direct plasma polymerization. In contrast, see

co-pending U.S. Patent Application Serial No. 09/157840, filed September 21, 1998 by P. France et al.,  
300 titled DURABLY WETTABLE POLYMERIC WEBS PREPARED USING A REMOTE PLASMA  
POLYMERIZATION PROCESS, which describes a process for making durably wettable webs using  
"remote" plasma polymerization.) The electrons or ions created in the plasma bombard the web's surface,  
abstracting atoms or breaking bonds, creating free radicals. These free radicals are unstable and seek to  
satisfy a more stable state by reacting with free radicals or groups within the plasma gas, also establishing  
305 new moieties on the surface of the web. In addition, the energetic electrons in the glow discharge fragment  
the molecules in the gas phase, leading to complex chemical reactions that result in a thin hydrophilic  
coating being deposited on at least one surface of the web.

Typically, and preferably, before plasma deposition of the hydrophilic coating onto the web, an  
initial step is performed. The purpose of this step is to clean the web's surface to promote adhesion of the  
310 subsequently deposited thin hydrophilic coating. Cleaning may be accomplished by subjecting the web's  
surface to radiation (herein referred to as radiation cleaning) from an energy source including but not  
limited to, infra red, electron beam, thermionic or ultra violet radiation or by plasma cleaning. Apparatuses  
that are suitable as energy sources in the present invention are disclosed in U.S. Patent No. 4,842,893  
issued to Yializis on Apr. 29, 1988. In the radiation cleaning embodiment, the radiation source is  
315 preferably a gas discharge electron beam gun. The gun directs a flow of electrons through a emitter  
window onto the web's surface, thereby abstracting atoms or breaking bonds, thus creating free radicals.  
These free radicals are unstable and seek to satisfy a more stable state thus they serve as bonding sites for  
the monomers that are used to produce the web's hydrophilic coating. Cleaning is controlled by matching  
the electron beam voltage to the dielectric thickness or depth of cleaning that is desired. For example, a 10  
320 Kv electron voltage will penetrate to a web depth of about 1 micron.

In the plasma cleaning embodiment, the gases are usually either Ar alone, O<sub>2</sub> alone, or mixtures  
(e.g., 1:1 ratio) of Ar and O<sub>2</sub>. Gas flow rates are typically in the range of about 20 to about 100 sccm  
(standard cc/min), preferably about 40 to about 80 sccm, and most preferably about 50 to about 60 sccm.  
RF power is approximately 1100 watts, and process pressure is about 0.040 Torr.

325 After the optional initial step, the next step is the plasma deposition of the hydrophilic coating, as  
described above and in more detail in the examples below. Often, but not always, a step subsequent to the  
CO<sub>2</sub> and N<sub>2</sub>O surface treating step is used to enhance the durability or uniformity of the plasma coating.  
Useful process gases are Ar and/or O<sub>2</sub>. Process times are usually about 1 to about 3 minutes, with about 2  
minutes typically being optimum. Gas flows range from about 40 to about 250 sccm, with process  
330 pressures from about 0.200 to about 0.400 Torr, and RF input power from about 150 to about 1500 watts.

The materials useful as polymeric films to be plasma treated to provide a hydrophilic coating will  
be derived from thermoplastic polymers. In general, the term "thermoplastic polymer" is used herein to  
mean any thermoplastic polymer which can be used for the preparation of films. Examples of  
thermoplastic polymers include, by way of illustration only, end-capped polyacetals, such as  
335 poly(oxymethylene) or polyformaldehyde, poly(trichloroacetaldehyde), poly(n-valeraldehyde),  
poly(acetaldehyde), poly(propionaldehyde), and the like; acrylic polymers, such as polyacrylamide,

poly(acrylic acid), poly(methacrylic acid), poly(ethyl acrylate), poly(methyl methacrylate), and the like; fluorocarbon polymers, such as poly(tetrafluoroethylene), perfluorinated ethylene-propylene copolymers, ethylene-tetrafluoroethylene copolymers, poly(chlorotrifluoroethylene), ethylene-chlorotrifluoroethylene copolymers, poly(vinylidene fluoride), poly(vinyl fluoride), and the like; polyamides, such as poly(6-aminocaproic acid) or poly( $\epsilon$ -caprolactam), poly(hexamethylene adipamide), poly(hexamethylene sebacamide), poly(11-aminoundecanoic acid), and the like; polyaramides, such as poly(imino-1,3-phenyleneiminoisophthaloyl) or poly(m-phenylene isophthalamide), and the like; polyarylenes, such as poly-p-xylylene, poly(chloro-p-xylylene), and the like; polyaryl ethers, such as poly(oxy-2,6-dimethyl-1,4-phenylene) or poly(p-phenylene oxide), and the like; polyaryl sulfones, such as poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene), poly(sulfonyl-1,4-phenyleneoxy-1,4-phenylene-sulfonyl-4,4'-biphenylene), and the like; polycarbonates, such as poly(bisphenol A) or poly(carbonyldioxy-1,4-phenylene-isopropylidene-1,4-phenylene), and the like; polyesters, such as poly(ethylene terephthalate), poly(tetramethylene terephthalate), poly(cyclohexylene-1,4-dimethylene terephthalate) or poly(oxymethylene-1,4-cyclohexyl-enemethyleneoxyterephthaloyl), and the like; polyaryl sulfides, such as poly(p-phenylene sulfide) or poly(thio-1,4-phenylene), and the like; polyimides, such as poly(pyromellitimido-1,4-phenylene), and the like; polyolefins, such as polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, polychloroprene, polyacrylonitrile, poly(vinyl acetate), poly(vinylidene chloride), polystyrene, and the like; copolymers of the foregoing, such as acrylonitrile-butadiene-styrene (ABS) copolymers, and the like.

Preferred polymers are polyolefins and polyesters, with polyolefins being more preferred. Even more preferred are those polyolefins which contain only hydrogen and carbon atoms and which are prepared by the addition polymerization of one or more unsaturated monomers. Examples of such polyolefins include, among others, polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, and the like. In addition, such term is meant to include blends of two or more polyolefins and random and block copolymers prepared from two or more different unsaturated monomers. Because of their commercial importance, the most preferred polyolefins are polyethylene and polypropylene.

In addition to polymeric films, webs that can be used to produce the durably wettable, liquid pervious webs of the present invention include but are not limited to spun bonded, hydroentangled, needled and polymericly bound nonwovens. Suitable nonwoven webs are typically formed from organic textile fibers including but not limited to cotton, wool, wood, jute, viscous rayon, nylon, polyester, polyolefins, carbon, or mixtures thereof. Inorganic fibers such as glass and metal can be used alone or in combination or further combined with organic fibers. In the case of staple fibers, fiber length varies from about 1/4 inch to about 2 or more inches. In the case of spun bonded webs, the fiber lengths are indefinite. The staple fibers used in hydroentangled, needled and polymericly bound nonwovens are processed through conventional textile machinery.

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375 For example, in producing a polymericly bound, nonwoven web, a carding machine may be used to form a continuous length of rather two-dimensional loosely associated fibers known as a carded web. These webs may be assembled to form a multiple layer or three-dimensional fibrous web of significant weight, e.g., from about several grams to thousands of grams per yard. In continuous nonwoven fibrous webs, the textile fibers are arrayed at various angles to the lengthwise axis of the web. When a web is  
380 formed by the action of a carding machine, the fibers are usually predominantly oriented in the machine direction and, on the other hand, isotropic webs may be formed such as by air-laying. The fibrous webs described above are typically impregnated with a polymeric binding agent (polymericly bound). In a preferred form, the polymeric binders are applied as emulsions of acrylic, polyvinylacetate, or similar polymeric nature, and mixtures thereof. Preferably, the fibers are unwoven and substantially haphazardly  
385 oriented and adhesively bonded together with polymeric binder.

Hydroentangled and needled webs are distinct from polymericly bound webs as they rely principally on the physical entanglement of their fibers to provide web integrity. In contrast to polymericly bound and physically entangled webs, spun bond webs typically are composed of fibers of infinite length that are bound together through solvent or melt processes.

390 As indicated, the webs may be in the form of a flat film or may be a previously apertured three dimensional film. The coatings are durable and increase the surface energy of the web to render the treated web more wettable. The coating is durable, in that it is maintained over time, even after exposure to water or other aqueous liquids. In this regard, the webs of the present invention are described in one respect in terms of their ability to remain wettable over time and/or after exposure to liquids. The ability to remain  
395 wettable over time is assessed by measuring the web's Post Aging contact angle. This measurement involves storing the treated web at 60° C for 16 hours, to artificially age the treated web, before measuring contact angle. The ability to remain wettable after exposure to liquids is assessed by measuring the web's Post Washing contact angle. This measurement involves placing a 2 in. x 2 in. sample of treated web in a 250 ml water bath at 65°C for 90 sec. with vigorous agitation prior to measuring contact angle. Procedures  
400 and devices for measuring contact angle between a liquid and a web surface are well known in the art. However, water contact angle, measured with a goniometer (Model # 100-00, Rame-Hart, Inc., Mountain Lakes, NJ), is used to assess the web wettability of the present invention. All contact angle measurements are reported as the average measurements on 3 samples.

In one aspect, the treated web of the present invention will have a Post Aging contact angle that is  
405 not more than about 60 degrees greater than the treated web's Pre Aging contact angle (i.e., the contact angle as measured before storage at 60°C for 16 hours). Preferably, the treated web will have a Post Aging contact angle that is not more than about 40 degrees, more preferably not more than about 20 degrees, still more preferably not more than about 10 degrees, greater than the Pre Aging contact angle. In another respect, the treated web of the present invention will have a Post Washing contact angle that is not more  
410 than about 60 degrees greater than the treated web's Pre Washing contact angle (i.e., the contact angle as measured before the treated web is placed in a 250 ml water bath at 65° C for 90 sec with vigorous agitation). In this regard, the treated web will preferably have a Post Washing contact angle that is not

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more than about 40 degrees, more preferably not more than about 20 degrees, still more preferably not more than about 10 degrees, greater than the Pre Washing contact angle. In a preferred aspect, the treated web of the present invention will exhibit both the Post Aging and Post Washing requirements discussed above.

The treated webs of the present invention will exhibit either (preferably both) a Post Aging or a Post Washing contact angle of less than about 90 degrees, preferably not more than about 70 degrees, more preferably not more than about 50 degrees, still more preferably not more than about 30 degrees, and most preferably not more than about 20 degrees.

## II Absorbent Articles

As used herein, the term "absorbent article" refers generally to devices used to absorb and contain body exudates, and more specifically refers to devices which are placed against or in proximity to the body of the wearer to absorb and contain the various exudates discharged from the body. The term "absorbent article" is intended to include diapers, catamenial pads, tampons, sanitary napkins, incontinent pads, training pants and the like, as well as wipes, bandages and wound dressings. The term "disposable" is used herein to describe absorbent articles which are not intended to be laundered or otherwise restored or reused as an absorbent article (i.e., they are intended to be discarded after limited use, and, preferably, to be recycled, composted or otherwise disposed of in an environmentally compatible manner). A "unitary" absorbent article refers to absorbent articles which are formed as a single structure or as separate parts united together to form a coordinated entity so that they do not require separate manipulative parts such as a separate holder and pad.

It is to be understood that the overall size, shape, and/or configuration of the absorbent article, if any, into which the treated webs according to the present invention are incorporated, or utilized in conjunction with, have no criticality or functional relationship to the principles of the present invention. Such parameters, however, must be considered along with the intended liquid and intended functionality when determining appropriate web configurations.

In addition to the treated webs of the present invention, absorbent articles will also comprise an absorbent core for retention of any absorbed body liquids. Exemplary absorbent structures for use as the absorbent core in the present invention are described in U.S. Patent No. 4,950,264 issued to Osborn on August 21, 1990; U.S. Patent No. 4,610,678 issued to Weisman et al. on September 9, 1986; U.S. Patent No. 4,834,735 issued to Alemany et al. on May 30, 1989; European Patent Application No. 0 198 683, the Procter & Gamble Company, published October 22, 1986 in the name of Duenk et al.; U.S. Patent No. 4,673,402 issued to Weisman et al. on June 16, 1987; and U.S. Patent No. 4,888,231 issued to Angstadt on December 19, 1989. The absorbent core may further comprise the dual core system containing an acquisition/distribution core of chemically stiffened fibers positioned over an absorbent storage core as detailed in U.S. Patent No. 5,234,423, entitled "Absorbent Article With Elastic Waist Feature and Enhanced Absorbency" issued to Alemany et al., on August 10, 1993; and in U.S. Patent No. 5,147,345, entitled

"High Efficiency Absorbent Articles For Incontinence Management" issued to Young, LaVon and Taylor on September 15, 1992. The disclosure of all of these patents is incorporated herein by reference.

A preferred embodiment of a unitary disposable absorbent article made in accordance herewith is a catamenial pad, or sanitary napkin. As used herein, the term "sanitary napkin" refers to an absorbent article which is worn by females adjacent to the pudendal region, generally external to the urogenital region, and which is intended to absorb and contain menstrual liquids and other vaginal discharges from the wearer's body (e.g., blood, menses, and urine). Interlabial devices which reside partially within and partially external to the wearer's vestibule are also within the scope of this invention. Suitable feminine hygiene articles are disclosed in U.S. Patent No. 4,556,146, issued to Swanson et al. on Dec. 3, 1985, U.S. Patent No. 4,589,876, issued to Van Tilburg on April 27, 1993, U.S. Patent No. 4,687,478, issued to Van Tilburg on Aug. 18, 1987, U.S. Patent No. 4,950,264, issued to Osborn, III on Aug. 21, 1990, U.S. Patent No. 5,009,653, issued to Osborn, III on April 23, 1991, U.S. Patent 5,267,992, issued to Van Tilburg on Dec. 7, 1993, U.S. Patent No. 5,389,094, issued to Lavash et al. on Feb. 14, 1995, U.S. Patent No. 5,413,568, issued to Roach et al. on May 9, 1995, U.S. Patent No. 5,460,623, issued to Emenaker et al. on Oct. 24, 1995, U.S. Patent No. 5,489,283, issued Van Tilburg on Feb. 6, 1996, U.S. Patent No. 5,569,231, issued to Emenaker et al. on Oct. 29, 1996, and U.S. Patent No. 5,620,430, issued to Bamber on April 15, 1997, the disclosure of each of which is incorporated by reference herein.

In a preferred embodiment of the present invention, the sanitary napkin has two flaps each of which are adjacent to and extend laterally from the side edge of the absorbent core. The flaps are configured to drape over the edges of the wearer's panties in the crotch region so that the flaps are disposed between the edges of the wearer's panties and the thighs. The flaps serve at least two purposes. First, the flaps help serve to prevent soiling of the wearer's body and panties by menstrual liquid, preferably by forming a double wall barrier along the edges of the panty. Second, the flaps are preferably provided with attachment means on their garment surface so that the flaps can be folded back under the panty and attached to the garment facing side of the panty. In this way, the flaps serve to keep the sanitary napkin properly positioned in the panty. The flaps can be constructed of various materials including materials similar to the topsheet, backsheet, tissue, or combination of these materials. Further, the flaps may be a separate element attached to the main body of the napkin or can comprise extensions of the topsheet and backsheet (i.e., unitary). A number of sanitary napkins having flaps suitable or adaptable for use with the sanitary napkins of the present invention are disclosed in U.S. Patent No. 4,687,478 entitled "Shaped Sanitary Napkin With Flaps", which issued to Van Tilburg on August 18, 1987; and U.S. Patent No. 4,589,876 entitled "Sanitary Napkin", which issued to Van Tilburg on May 20, 1986. The disclosure of each of these patents is hereby incorporated herein by reference.

In a preferred embodiment of the present invention, an acquisition layer(s) may be positioned between the topsheet and the absorbent core. The acquisition layer may serve several functions including improving wicking of exudates over and into the absorbent core. There are several reasons why the improved wicking of exudates is important, including providing a more even distribution of the exudates throughout the absorbent core and allowing the sanitary napkin to be made relatively thin. The wicking

referred to herein may encompass the transportation of liquids in one, two or all directions (i.e., in the x-y plane and/or in the z-direction). The acquisition layer may be comprised of several different materials including nonwoven or woven webs of synthetic fibers including polyester, polypropylene, or polyethylene; natural fibers including cotton or cellulose; blends of such fibers; or any equivalent materials or combinations of materials. Examples of sanitary napkins having an acquisition layer and a topsheet are more fully described in U.S. Patent No. 4,950,264 issued to Osborn and U.S. Patent Application Serial No. 07/810,774, "Absorbent Article Having Fused Layers", filed December 17, 1991 in the names of Cree, et al. The disclosures of each of these references are hereby incorporated herein by reference. In a preferred embodiment, the acquisition layer may be joined with the topsheet by any of the conventional means for joining webs together, most preferably by fusion bonds as is more fully described in the referenced Cree application.

Catamenial pads may be constructed as follows. Onto silicone-coated release paper a spiral pattern of H2031 Findlay hot melt adhesive is applied at 0.04 g/in<sup>2</sup>. This adhesive layer is transferred onto the top (wearer-facing) side of a secondary topsheet by rolling the secondary topsheet and coated release paper together with a hand roller. The secondary topsheet is formed of a nonwoven material known as Fort James Airlaid Tissue, Grade 817, commercially available from the Fort James Corp. of Green Bay, Wisconsin. A topsheet of the present invention is applied to the adhesive side of the secondary topsheet and the two are bonded by gently pressing them together with a hand roller. Two strips of one-quarter-inch double-sided tape are applied along both long edges of a polyethylene backsheet. The absorbent core is added to construct the complete absorbent structure.

As used herein, the term "diaper" refers to a garment generally worn by infants and incontinent persons that is worn about the lower torso of the wearer. It should be understood, however, that the present invention is also applicable to other absorbent articles such as incontinent briefs, incontinent pads, training pants, diaper inserts, facial tissues, paper towels, and the like. In general, a diaper of the present invention will comprise a liquid pervious topsheet of the present invention; a liquid impervious backsheet joined with the topsheet; and an absorbent core positioned between the topsheet and the backsheet. Additional structural features such as elastic members and fastening means for securing the diaper in place upon a wearer (such as tape tab fasteners) may also be included.

While the topsheet, the backsheet, and the absorbent core can be assembled in a variety of well known configurations, a preferred diaper configuration is described generally in U.S. Patent No. 3,860,003 (Buell), issued January 14, 1975, the disclosure of which is incorporated by reference. Alternatively, preferred configurations for disposable diapers herein are also disclosed in U.S. Patent No. 4,808,178 (Aziz et al.), issued February 28, 1989; U.S. Patent No. 4,695,278 (Lawson), issued September 22, 1987; and U.S. Patent No. 4,816,025 (Foreman), issued March 28, 1989, the disclosures of each of these patents hereby being incorporated herein by reference. Suitable incontinence articles for adult wearers are disclosed in U.S. Patent No. 4,253,461 issued to Strickland, et al. on March 3, 1981; U.S. Patent Nos. 4,597,760 and 4,597,761 issued to Buell; U.S. Patent No. 4,704,115; U.S. Patent No. 4,909,802 issued to Ahr, et al.; U.S. Patent No. 4,964,860 issued to Gipson, et al. on October 23, 1990; and in U.S. Patent



Application Serial No. 07/637,090 filed by Noel, et al. on January 3, 1991 (PCT Publication N . WO 92/11830 published on July 23, 1992). The disclosure of each of these references is incorporated herein.

530 The absorbent core of the diaper is positioned between the topsheet and the backsheet. The absorbent core can be manufactured in a wide variety of sizes and shapes (e.g., rectangular, hourglass, asymmetrical, etc.). The total absorbent capacity of the absorbent core should, however, be compatible with the design liquid loading for the intended use of the absorbent article or diaper. Further, the size and absorbent capacity of the absorbent core can vary to accommodate wearers ranging from infants through adults.

535 As indicated, the absorbent core may include a liquid distribution member. In a preferred configuration, the absorbent core preferably further includes an acquisition layer or member in liquid communication with the liquid distribution member and located between the liquid distribution member and the topsheet. The acquisition layer or member may be comprised of several different materials including nonwoven or woven webs of synthetic fibers including polyester, polypropylene, or polyethylene, natural  
540 fibers including cotton or cellulose, blends of such fibers, or any equivalent materials or combinations of materials.

In a preferred embodiment, the diaper will comprise elasticized leg cuffs. The elasticized leg cuffs can be constructed in a number of different configurations, including those described in U.S. Patent No. 3,860,003; U.S. Patent No. 4,909,803, issued to Aziz et al. on Mar. 20, 1990; U.S. Patent No. 4,695,278,  
545 issued to Lawson on Sep. 22, 1987; and U.S. Patent No. 4,795,454, issued to Dragoo on Jan. 3, 1989, each being incorporated herein by reference.

In use, the diaper is applied to a wearer by positioning the back waistband region under the wearer's back, and drawing the remainder of the diaper between the wearer's legs so that the front waistband region is positioned across the front of the wearer. The tape-tab or other fasteners are then secured  
550 preferably to outwardly facing areas of the diaper.

### III. Examples

The following examples are illustrative and are not meant as a limitation of the invention disclosed and claimed herein. With respect to Example 2, the mass flow controller used to deliver the silicon-containing monomer compound for the deposition processes was calibrated for the flow rate of HMDSO.

555 The flow rates of other gases were calculated based on the specific heats of the respective gases. The accuracy of the mass flow controllers in these cases is  $\pm 5\%$  or better.

#### Example 1

560 This example illustrates the plasma treatment process and benefit of this invention in applying a permanent hydrophilic coating to a flat polyethylene film. Flat polyethylene (PE) film having a 1 mil average thickness is obtained from Tredegar Film Products, Inc. (Terre Haute, IN) with material composition designation code X-8318-1. Three-step plasma treatments are conducted in a plasma reactor (Advanced Plasma System, Model D, radio frequency (RF) : 40 KHz), with the gas input and process conditions indicated in Table 1.

Table 1

Step #	Gas Input *	Flow Rate (sccm)**	RF Power (Watt)	Treatment Time (min)
1	Ar/O <sub>2</sub>	2/73	500	2
2	Ar/O <sub>2</sub> /HMDSO	2/73/50	500	10
3	Ar/O <sub>2</sub>	2/73	500	1

565 \*: Ar: Argon; O<sub>2</sub>: oxygen; HMDSO: hexamethyl disiloxane

\*\* : sccm: standard cm<sup>3</sup>/minute

570 The resulting plasma treated web samples are then tested for surface wettability both before and after rapid aging conditions. Rapid aging condition refers to conditioning the web sample at 60° C for 16 hours prior to wettability measurement. Water contact angle, measured with a goniometer (Model # 100-00, Rame-Hart, Inc., Mountain Lakes, NJ), is used to assess web wettability. Strong wetting durability of HMDSO-derived plasma coating is established, as demonstrated by comparable contact angles seen between pre-aged and post-aged samples (see Table 2).

Table 2

Sample	Water Contact Angle* (degrees)	
	Pre-Aged	Post-Aged
Untreated PE film	96 (3)	96 (3)
HMDSO-plasma treated PE web	26 (1)	26 (3)

575 \*: Contact angle measured 3 times on the same treated web is averaged and standard deviation is reported in parenthesis.

#### Example 2

This example illustrates the alternate plasma treatment process and benefit of this invention in applying a permanent hydrophilic coating to a flat PE film. Flat PE film having a 1 mil average thickness is obtained from Tredegar Film Products, Inc. (Terre Haute, IN) with material composition designation

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580 code X-8318-1. Three-step plasma treatments are conducted in a plasma reactor (Plasma Science PS0500D), with gas input and process conditions indicated in Table 3.

Table 3

Step #	Gas Input **	Flow Rate (sccm)*	RF Power (Watt)	Treatment Time (min)
1	Ar	58	1080	1
2	Ar/O <sub>2</sub> /HMDSO	43/1560/52	1200	2
3	N <sub>2</sub> O/CO <sub>2</sub>	200/207	1325	2

\* sccm : standard cm<sup>3</sup>/minute

\*\* Ar: Argon; O<sub>2</sub>: oxygen; HMDSO: hexamethyl disiloxane; N<sub>2</sub>O: nitrous oxide;

585 CO<sub>2</sub>: carbon dioxide

The resulting plasma treated web samples are then evaluated for surface wettability before and after the water wash test. Water wash test refers to immersing a 2 in. x 2 in. web sample in a 250 ml water bath at 65° C for 90 sec with vigorous agitation (with a Teflon coated stir bar). Water contact angle, measured with a goniometer (model # 100-00, Rame-Hart, Inc., Mountain Lakes, N.J.), is used to assess the webs' wettability. Strong wetting durability of HMDSO-derived plasma coating is established, as is demonstrated by comparing contact angle between pre-washed and post-washed samples (see Table 4).

Table 4

Sample	Water Contact Angle * (degrees)	
	Pre-washed	Post-washed
Untreated PE Film	96 (3)	96 (3)
HMDSO-plasma treated PE Web	7 (1)	14 (1)

\*: contact angle measured 3 times on the same film/web is averaged and standard deviation is reported in parenthesis.

595 While specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

What is claimed is:

1. A direct plasma polymerization process for making a durably wettable, liquid pervious web for use as a topsheet in an absorbent article, the process comprising:
  - (i) introducing a web to a plasma reaction zone; and
  - (ii) coating at least one of the surfaces of the web with a coating of polymerized monomers, wherein the coating is less than 2.5 microns thick and is derived from a monomer gas stream that will provide a hydrophilic coating upon plasma polymerization;said process characterized in that the web is selected from the group consisting of polymeric films, apertured polymeric films, nonwovens and apertured nonwovens; wherein the polymerized monomers cause at least one surface of the web to become durably-wettable.
2. The process of Claim 1 wherein at least one surface of the durably-wettable, liquid pervious web has a Post Aging contact angle that is not more than 60 degrees greater than the Pre Aging contact angle, preferably not more than 40 degrees greater than the Pre Aging contact angle and most preferably not more than 20 degrees greater than the Pre Aging contact angle.
3. The process of any preceding claim wherein at least one surface of the durably-wettable, liquid pervious web has a Post Washing contact angle that is not more than 60 degrees greater than the Pre Washing contact angle, preferably is not more than 40 degrees greater than the Pre Washing contact angle and most preferably not more than 20 degrees greater than the Pre Washing contact angle.
4. The process of any preceding claim wherein the process further comprises the step of cleaning the surface of the web by exposing the surface to plasma conditions or an energy source selected from the group consisting of infra red, electron beam, thermionic or ultra violet radiation and mixtures thereof, prior to introduction of the monomer gas stream of step (ii).
5. The process of Claim 4 wherein the step of cleaning the surface of the web by exposing the web to plasma conditions comprises introduction of a gas stream comprising a material selected from the group consisting of Ar, O<sub>2</sub>, and mixtures thereof.
6. The process of any preceding claim wherein the process comprises the step of further modifying the hydrophilic surface by introducing the web formed in step (ii) to a surface modifying gas stream, the gas stream comprising N<sub>2</sub>O and CO<sub>2</sub>; or an energy source selected from the group consisting of infra red, electron beam, thermionic or ultra violet radiation and mixtures thereof.

7. The process of any preceding claim further comprising a final step comprising aperturing the coated web.
8. The process of any preceding claim wherein the polymeric film is derived from a material selected from the group consisting of polyolefins, polyesters, and mixtures thereof.
9. The process of Claim 8 wherein the polymeric film is derived from a material selected from the group consisting of polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, blends thereof, random copolymers thereof, and block copolymers thereof.
10. The process of any preceding claim wherein the monomer gas stream comprises a monomer selected from the group consisting of (i) silanes of the formula  $\text{Si}(\text{R})_4$ , where each R is the same or different and is selected from H; a  $\text{C}_1\text{-C}_8$  linear or branched alkyl or alkoxy; a  $\text{C}_6\text{-C}_{10}$  aryl, unsubstituted or substituted with  $\text{C}_1\text{-C}_4$  linear or branched alkyl; a vinyl radical; or a  $\text{C}_3\text{-C}_5$  allyl radical; provided not more than two R groups are H; (ii) organosilicones of the formula  $\text{R}'\text{R}''\text{R}''' \text{Si}[-\text{O}-\text{Si}(\text{R}')(\text{R}'')-]_n-\text{R}'''$ , where  $\text{R}'$ ,  $\text{R}''$  and  $\text{R}'''$  can be the same or different and are  $\text{C}_1\text{-C}_8$  linear or branched alkyl or alkoxy, wherein  $\text{R}'$  and  $\text{R}''$  may be hydrogen provided that no more than 50% of the  $\text{R}'$  and  $\text{R}''$  groups are hydrogen, and n is 1, 2 or 3; and (iii) mixtures thereof; and wherein said monomer gas stream further comprises oxygen when said monomer of said gas stream consists only of said silanes.
11. The process of Claim 10 wherein the monomer gas stream comprises a monomer selected from the group consisting hexamethyldisiloxane, methyltrimethoxy silane, vinyltrimethoxy silane, vinyltriethoxy silane and oxygen, ethylmethoxy silane, ethyltrimethoxy silane, tetraethoxy silane, cyclohexylmethyl-dimethoxy silane, dicyclopentyl-dimethoxy silane, phenyltriethoxy silane, diphenyldimethoxy silane, tetramethyldisiloxane, hexamethyltrisiloxane, and mixtures thereof; and wherein said monomer gas stream further comprises oxygen when said monomer of said gas stream consists only of said silanes.
12. The process of any preceding claim wherein the gas of the monomer gas stream is ionized via pulsation of high frequency microwaves or radiowaves.
13. An absorbent article characterized in that said absorbent article comprises a durably wettable, liquid pervious topsheet produced by the processes of any one of the preceding claims.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 99/21709

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B05D7/24 D06M10/02 D06M10/08 D06M10/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D D06M A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YOSHIMURA K ET AL: "PREPARATION OF HYDROPHILIC PLASMA-POLYMERS DERIVED FROM OXYGEN- CONTAINING ORGANIC MONOMERS" JOURNAL OF APPLIED POLYMER SCIENCE,US,JOHN WILEY AND SONS INC. NEW YORK, vol. 59, no. 6, 7 February 1996 (1996-02-07), pages 1033-1042, XP000551855 ISSN: 0021-8995 page 1034, left-hand column, line 12 - line 20 — —/—	1,8,12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

14 February 2000

Date of mailing of the international search report

22/02/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 051 epo nl,  
Fax (+31-70) 340-3018

Authorized officer

Brothier, J-A

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/21709

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI  Section Ch, Week 198931  Derwent Publications Ltd., London, GB;  Class A35, AN 1989-224504  XP002130415  &amp; JP 01 161026 A (TAKAMATSU YUSHI KK),  23 June 1989 (1989-06-23)  abstract</p>	1,6,8
X	<p>DATABASE WPI  Section Ch, Week 199338  Derwent Publications Ltd., London, GB;  Class A35, AN 1993-297840  XP002130416  &amp; JP 05 209072 A (JAPAN SYNTHETIC RUBBER  CO LTD), 20 August 1993 (1993-08-20)  abstract</p>	1,2,12
X	<p>DATABASE WPI  Section Ch, Week 198650  Derwent Publications Ltd., London, GB;  Class A14, AN 1986-329479  XP002130417  &amp; JP 61 246204 A (TOKAI PULP KK),  1 November 1986 (1986-11-01)  abstract</p>	1
P,X	<p>WO 99 05358 A (SAYERS IAN CHRISTISON  ;SCAPA GROUP PLC (GB))  4 February 1999 (1999-02-04)  the whole document</p>	1,10
P,X	<p>WO 99 39842 A (MOSER EVA MARIA ;EMPA ST  GALLEN EIDGENOESSISCHE (CH))  12 August 1999 (1999-08-12)  the whole document</p>	1,8
P,X	<p>EP 0 896 035 A (UNIV TEXAS)  10 February 1999 (1999-02-10)  the whole document</p>	1
A	<p>WO 95 04609 A (CIBA GEIGY AG ;KLING RENATE  &amp; LF (DE); SEIFERLING BERNHARD (DE); B)  16 February 1995 (1995-02-16)  page 15</p>	3
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Int. Application No.

PCT/US 99/21709

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>LEE S H ET AL: "PREPARATION AND CHARACTERIZATION OF THIN FILMS BY PLASMA POLYMERIZATION OF HEXAMETHYLDISILOXANE" THIN SOLID FILMS,CH,ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 325, no. 1/02, 18 July 1998 (1998-07-18), pages 83-86, XP000667948 ISSN: 0040-6090 the whole document</p>	10



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Information on patent family members

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